

July 17, 2015

Ms. Linda Wilson BP Refinery 2815 Indianapolis Blvd. Whiting, IN 46394

Subject: 2014 EPA Data Comparison of Integrated Sampling Methods to BP Whiting

**Fenceline AutoGC Air Monitors** 

Dear Linda:

Per our recent correspondence via email, I have asked my project team to evaluate the initial information provided to us regarding the Region 5 EPA VOC study conducted in the fall of 2014. Our general conclusions regarding initial report of results from the EPA VOC measurement methods study conducted at the Whiting Refinery is as follows:

- 1) The averages displayed in the presentation of results for the EPA study fall below our lowest calibration curve concentration level of 1 ppb-v, so the results should not be relied upon for reported concentration accuracy as one would for results within the calibrated range of the AutoGC at each fixed site. This data set contains a lot of extrapolated concentration data, especially from Sites 2 and 3.
- 2) The AutoGC chromatograms at the monitoring sites are occasionally influenced by the presence of other peaks within the benzene retention time (RT) window, an issue known as co-elution, and we take a conservative approach in integrating them when they overlap, which is likely to result in slight overestimation of the benzene concentration (examples provided in Attachment A, which is a working material only and not suitable for a presentation). This seems to be most prevalent at Site 1.
- 3) The co-elution issue in the benzene RT window has not been subject to further study because it was judged not to be detrimental to the goals of the Consent Decree. We would like to get the 60 compound EPA analysis results of canister data during the study to get a better view of what the potential co-eluting compound(s) could be, if they will share them. This is for our benefit as quality control information; we are not advocating a co-elution study at this time.



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- 4) The nature of the measurements is quite different, with two continuously integrated sampling methods (canisters/sorbent tubes) being compared to a 40 minute per hour sample trap, followed by desorption and analysis. Per the Consent Decree and the QAPP for the fence line project, we have a series of quality control samples that must be run on a regular basis at each site. This requires the AutoGC to be offline for several hours a day, while during the study the EPA samples were collecting continuously over their sampling periods. These two issues could make the difference in actual measurement time between the EPA and BP site on the order of 50-60% (24 hours a day for the EPA samples and 12-14 hours of actual sample acquisition time per day by the AutoGCs). The larger the database (and time period) under analysis, the better the agreement between mean concentration values should be, given no significant contributions due to a systematic bias.
- 5) The sorbent tubes and canisters were analyzed by GC/mass spectroscopy rather than GC/FID/PID (the AutoGC employed at BP), and mass spectroscopy has the advantage of being better able to identify and separate various compounds.
- 6) The distribution of concentrations is different at Sites 1 and 4 compared to Sites 2 and 3; 1 and 4 have a much wider distribution of concentrations than 2 and 3 (as shown in Attachment B, also a working material not suitable for presentation). This may be a factor to consider in evaluating the EPA table of benzene averages by site comparing the three measurement methods.

We acknowledge that none of these issues individually presents an insurmountable problem, but want data users to be aware of the limitations of the potential comparisons of AutoGC data to sampling methods that employ off-site analytical techniques. Any thorough evaluation of such a comparison should account for the sample acquisition and analysis differences between methods, especially with a data set that averages sub-ppbv levels.

Our evaluation of the results also gives us further confidence that the goal of the Consent Decree to provide meaningful data to the public on a regular basis is being met. Please let me know if you would like for us to do any further evaluation work based on the EPA study.

Best Regards,

James Clarke

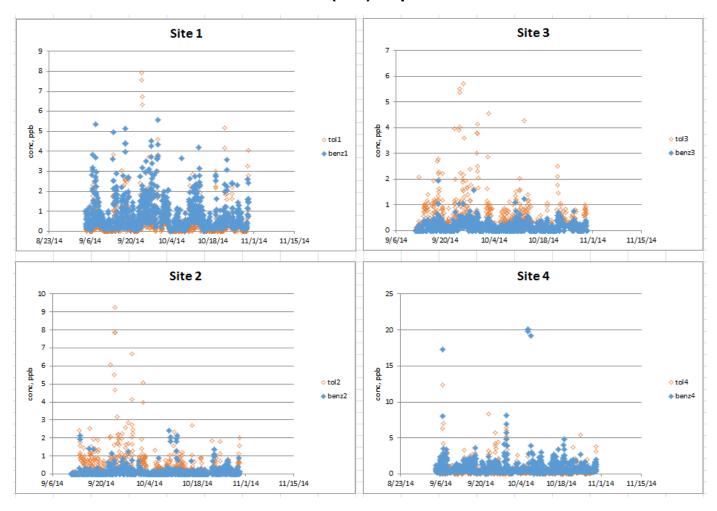
Senior Project Manager

James Clarke

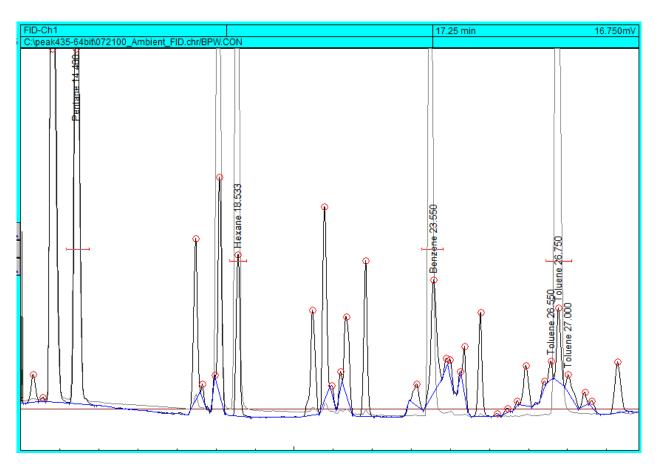
## **ATTACHMENT A**

**Co-elution Examples** 

## BPW Benzene and Toluene (FID) September and October 2014

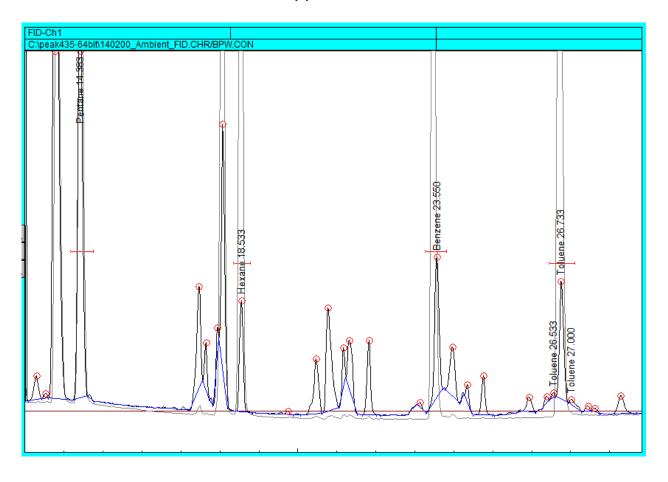


Site 1 9/7/15 21:00 5.4 ppb Benzene

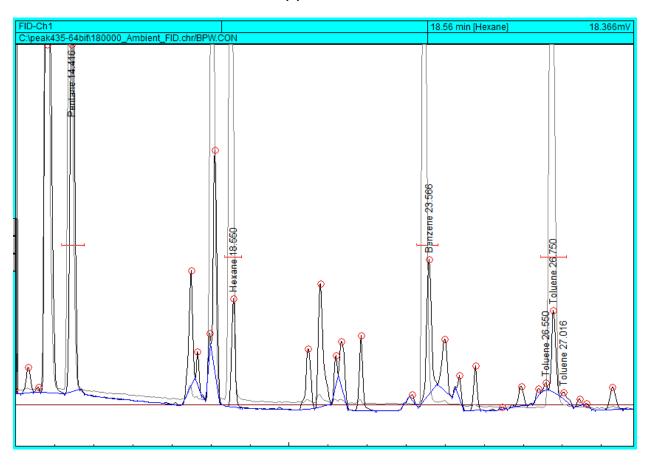


Benzene peak shape and very slightly late RT suggest possible coelution.

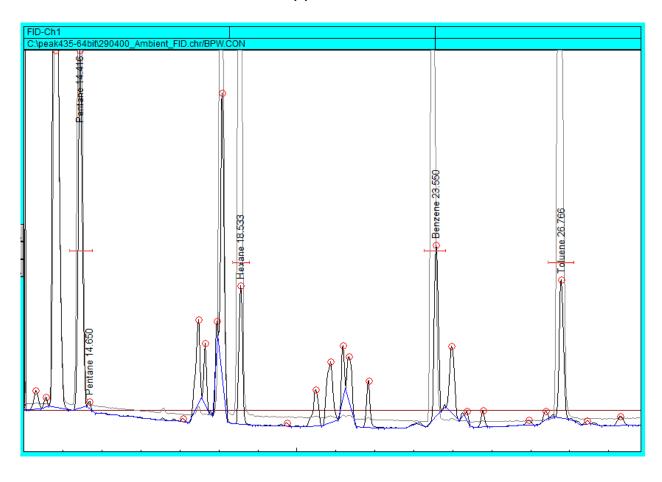
Site 1 9/14/15 02:00 5.0 ppb Benzene



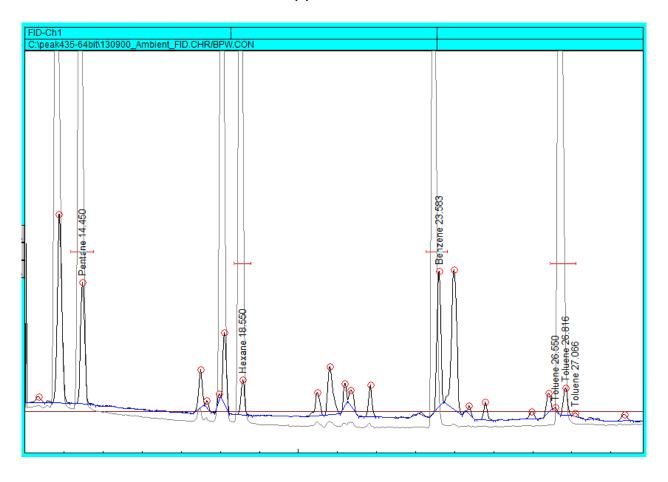
Site 1 9/18/15 00:00 5.2 ppb Benzene



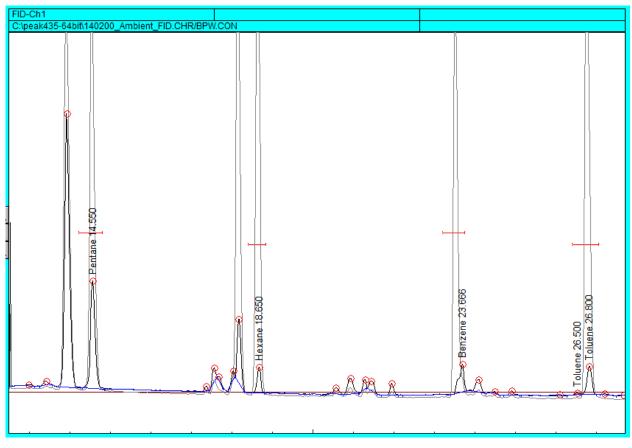
Site 1 9/29/15 04:00 5.6 ppb Benzene



Site 1 10/13/15 09:00 4.2 ppb Benzene

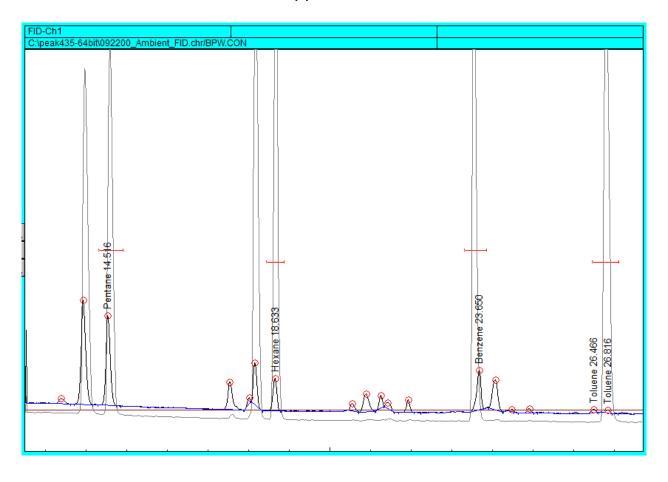


Site 2 9/14/15 02:00 2.1 ppb Benzene

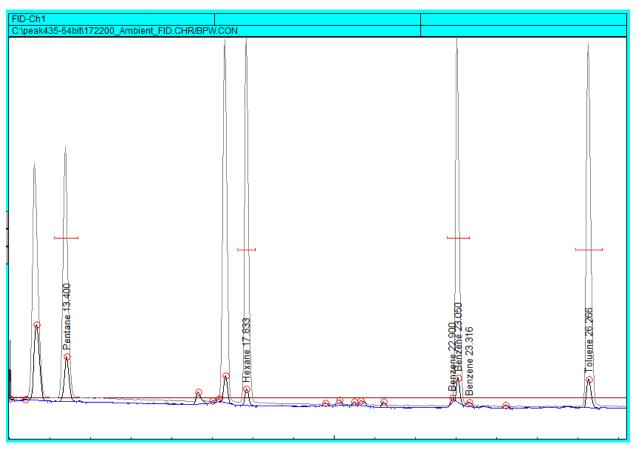


Apparent coelution for benzene, but max benzene reported for Sept/Oct 2014 was 2.4 ppb.

Site 2 10/9/15 22:00 2.4 ppb Benzene

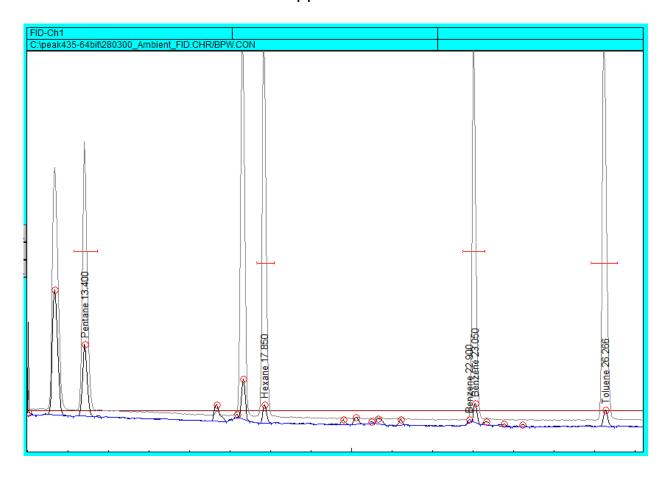


Site 3 9/17/15 22:00 1.9 ppb Benzene

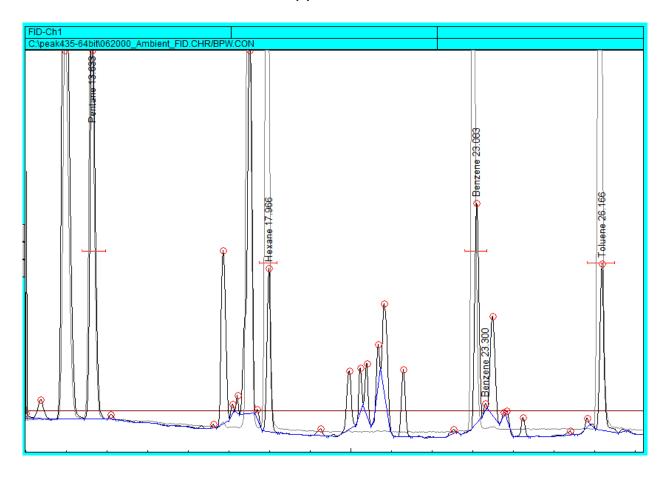


This was biggest benzene hit reported for Site 3 for Sept/Oct 2014.

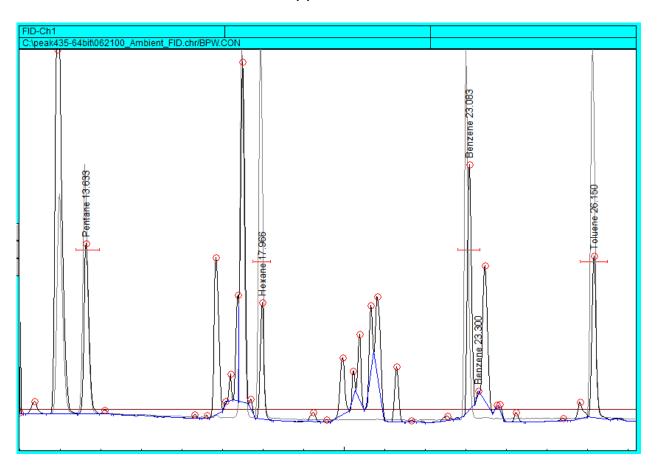
Site 3 9/28/15 03:00 1.6 ppb Benzene



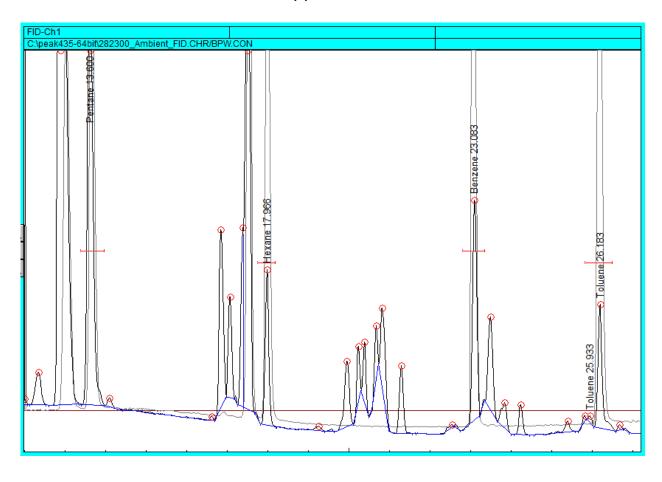
Site 4 9/6/15 20:00 8.0 ppb Benzene



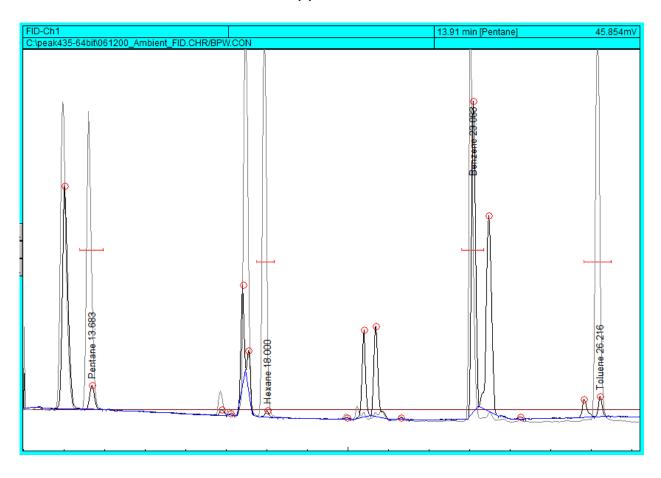
Site 4 9/6/15 21:00 17.3 ppb benzene



Site 4 9/28/15 23:00 8.1 ppb Benzene

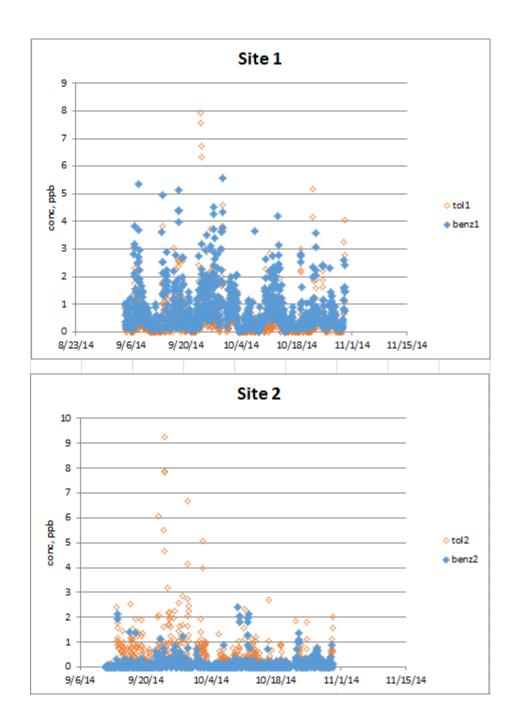


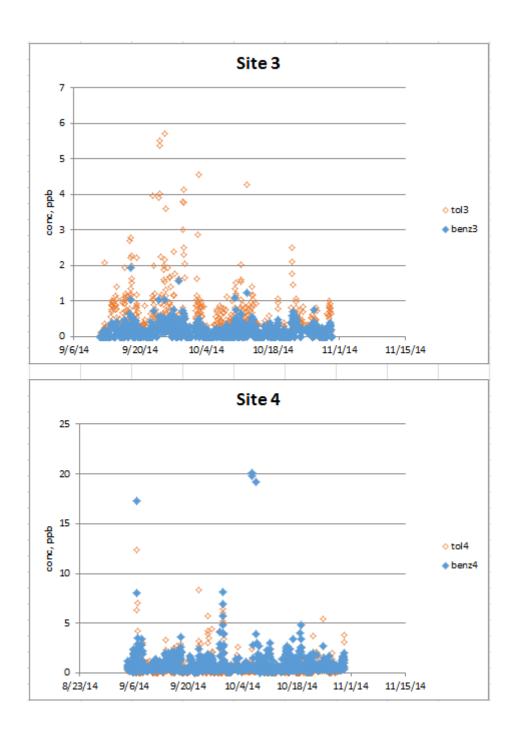
Site 4 10/6/15 12:00 20.2 ppb Benzene

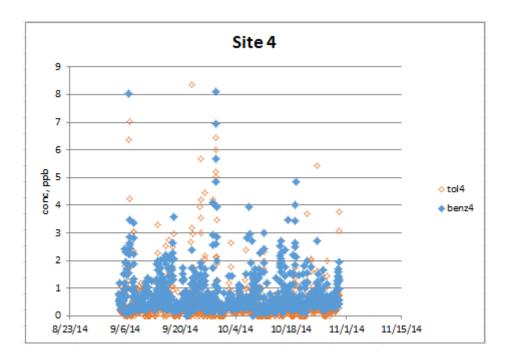


## **ATTACHMENT B**

**Distribution of AutoGC Concentrations by Monitoring Site** 







NOTE: lower y-axis scale than previous plot to show more detail